

Airborne Perfluorooctanoate May Be a Substantial Source Contamination in Kyoto Area, Japan

K. Harada,¹ S. Nakanishi,² N. Saito,³ T. Tsutsui,² A. Koizumi¹

¹ Department of Health and Environmental Sciences, Kyoto University School of Public Health, Kyoto, Japan

² Kyoto Prefectural Institute of Hygienic and Environmental Sciences, Kyoto, Japan

³ Research Institute for Environmental Sciences and Public Health of Iwate Prefecture, Morioka Iwate, Japan

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Perfluorochemicals (PFCs) such as PFOS (perfluorooctane sulfonate) or PFOA (perfluorooctanoate) are environmental contaminants posing special public health concerns because of their stability, long-term persistence and bio-accumulativeness in the environment. They have been used widely in lubricants, paints, cosmetics, firefighting foam and other applications.

PFOS and PFOA have been found in wildlife and humans (Kannan et al. 2002; Olsen et al. 2003; Harada et al. 2004). However, there were little information on environmental contamination and human exposure to PFCs. Recently, we have shown that drinking water is one of the major factors in human exposure to PFOA and PFOS in Japan (Saito et al. 2004). It seems to be one of major sources of exposure to PFOA and PFOS as well (Saito et al. 2004), but the extent of exposure from routes such as air, food, etc., remains unknown.

We have previously reported PFOS contamination of air-borne dust in Kyoto Japan, and found that exposure to PFOS from air-borne dust is much less in impact than from tap water (Harada et al. 2003; Sasaki et al. 2003). A survey on surface water in Japan revealed that PFOA contamination of water system was extensive around Kyoto (Saito et al. 2004).

The aim of the present study is to evaluate concentration levels of air-borne PFOA. This information is required to evaluate the importance of inhalation in human body load of PFOA. For this reason, we measured air-borne PFOA and PFOS contamination in Kyoto and Iwate, Japan. Two cities was selected because serum levels of PFOA suggests that the former is representative of highly contaminated areas, while the latter of low contaminated areas (Harada et al. 2004).

MATERIALS AND METHODS

Heptadecafluorooctane sulfonic acid potassium salt (FW.538.22), used as a standard for PFOS, and pentadecafluorooctanoic acid ammonium salt (FW.431.10), used as a standard for PFOA, were purchased from Fluka (Milwaukee, WI). The purity levels of PFOS and the PFOA used as standards were higher than 98%. We did not correct the reported concentrations according to purity. Methanol and acetonitrile were HPLC grades. The purity levels of

ammonium acetate was higher than 99%.

Air dust samples were collected in the town of Oyamazaki (Kyoto Pref., Japan) and Morioka City (Iwate Pref., Japan), as previously reported (Sasaki et al. 2003). Oyamazaki samples were collected every month from April 2001 to March 2002 at a sampling station. Morioka samples were collected on 16, 17, 18 and 20 July 2003. At Oyamazaki sampling station, approximately 1,400 m³ of air was collected over a period of 24 hours with vacuum sampler MODEL-120V (Kimoto Electric Co., Ltd. Osaka, Japan) from air-collecting orifices, which were located 1.5 m above ground level. Air dust particles were collected on a quartz membrane filter (PALLFLEX 2500QAT-UP, 8 x 10 in., Pallflex Products Corporation, USA). At Morioka sampling station, approximately 1,000 m³ of air was collected over a period of 24 hours, and a quartz membrane filter (ADVANTEC QR-100, 8 x 10 in., Advantec Toyo Kaisha, Ltd., Tokyo) was used. The sampling station is located on national road Route 171 in the town of Oyamazaki and on a local road in Morioka City. Route 171 is the one of the busiest trunk route in Japan. The filter samples were stored at room temperature, along with a blank, until analyzed.

An automated extraction system (Dionex AES 200, Accelerated Solvent Extractor) was used for extraction of PFOA and PFOS as previously reported (Sasaki et al. 2003). Halves of the filter samples were used. Extracted solutions were concentrated to 1 mL for analysis by LC/MS.

The details on LC/MS and quantification have been described previously (Saito et al. 2003; Saito et al. 2004). The methanol extracts (10 µl injection volume of the 1 mL extract) were chromatographed using HPLC with a flow rate of 0.2 mL/min as previously reported (Sasaki et al. 2003).

The PFOA and PFOS standards were mixtures of linear and branched isomers (approximately 80% linear). Because isomerically separated standards for PFOA and PFOS are not available, it was assumed that the response factors for branched and linear isomers are equivalent and that the standard mixture is representative of that identified in the samples.

Mass spectra were taken with an LC/MS system equipped with an orthogonal spray interface, employing electrospray ionization in the negative mode. The fragmentor voltages were 100 V for PFOA and 200 V for PFOS, and V cap voltages were 4000 V for both analytes. The nebulizer pressure was 50 psig, and the drying N₂ gas flow rate was 10.0 L/min. The selected ion monitoring (SIM) mode was employed for quantification of analytes. In the selected negative-ion mode monitoring of ions, the fragment ions for PFOA m/z 413 (C₇F₁₅CO₂⁻) and for PFOS m/z 499 (C₈F₁₇SO₃⁻) were monitored for quantification. To avoid interference and ensure complete selectivity, the fragment of PFOA, m/z 369 (fragment C₇F₁₅⁻) was monitored. The fragment of PFOS m/z 99 (fragment, FSO₃⁻) was also monitored. The lowest limits of detection (LOD) (ng) were calculated by measuring the blank silica fiber filters.

Spike and recovery experiments were performed to determine the precision and accuracy of the method. One set of spike and recovery experiments was performed using quartz membrane filters that contained known amounts of PFOA and PFOS. Six filter samples were spiked to a final concentration of 10 ng/mL PFOS and PFOA.

RESULTS AND DISCUSSION

Standard addition experiments revealed that the mean recoveries of PFOA and PFOS for air dust samples collected on the quartz membrane filters were 89.4 ± 3.91 , 98.0 ± 4.36 (% \pm S.D.), respectively (Table 1). The LOD of PFOA and PFOS were determined to be 0.138 (ng) for PFOA and 0.091 (ng) for PFOS in the samples, respectively, and the LOQ of PFOA and PFOS were 0.460 and 0.302 (ng) respectively (data not shown).

The PFOA and PFOS concentrations of all the samples were larger than the quantification limit. Most of the PFOA and PFOS concentrations of the air dust samples were significantly higher than in the blanks. To quantify the PFOA and PFOS concentration in air, we subtracted the background levels from the sample values. The annual geometric means (GM) (geometric standard deviation: GSD) of the PFOA and PFOS concentrations in the air (pg/m^3) were 262.8 (1.4), 5.2 (1.2) for the town of Oyamazaki and 2.0 (1.1), 0.7 (1.2) for Morioka City, respectively (Table 2). It was significantly higher in Oyamazaki than in Morioka for both PFOA and PFOS ($p < 0.01$). There was no significant difference of PFOS concentrations between in Morioka and Fukuchiyama, where PFOS concentrations are assumed to be typical of rural areas [$0.6 \text{ pg}/\text{m}^3$ (1.3) (Sasaki et al. 2003)].

Table 1. Recovery of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) using silica fiber filters ^{a)}

| Fortification concentration ^{b)} | | | | | | | |
|---|------------|----------------------------|--|--------------------|------------|----------------------------|--|
| Fortification (ng) | Found (ng) | PFOA | | Fortification (ng) | Found (ng) | PFOS | |
| | | Recovery (%) ^{c)} | | | | Recovery (%) ^{c)} | |
| 10.0 | 9.00 | 90.0 | | 10.0 | 9.72 | 97.2 | |
| 10.0 | 9.18 | 91.8 | | 10.0 | 10.18 | 101.8 | |
| 10.0 | 8.64 | 86.4 | | 10.0 | 9.28 | 92.8 | |
| 10.0 | 8.46 | 84.6 | | 10.0 | 9.50 | 95.0 | |
| 10.0 | 9.42 | 94.2 | | 10.0 | 10.30 | 103.0 | |
| Mean | 8.94 | 89.4 | | | 9.80 | 98.0 | |
| S.D.(n-1) | 0.39 | 3.9 | | | 0.44 | 4.4 | |
| CV(%) | 4.4 | 4.4 | | | 4.5 | 4.5 | |

a) Silica fiber filters (ADVANTEC QR-100) used for sampling air-borne dust.

b) 10 ng of PFOA and PFOS was added to the silica fiber filter paper (101.5x127mm).

c) Recovery (%) = (Found)*100/10

Table 2. perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) concentrations in Oyamazaki and Morioka.

| | Sampling Date | Dust | PFOA | PFOA in dust | PFOS | PFOS in dust |
|------------------|---------------|--------------------------|------------------------|----------------------|------------------------|----------------------|
| | | $\mu\text{g}/\text{m}^3$ | pg/m^3 | ng/g | pg/m^3 | ng/g |
| Oyamazaki | | | | | | |
| O1 | 2001.04.23 | 83 | 755 | 9049 | 6.62 | 79.3 |
| O2 | 2001.05.15 | 48 | 218 | 4580 | 7.99 | 168.0 |
| O3 | 2001.06.05 | 52 | 407 | 7881 | 5.95 | 115.4 |
| O4 | 2001.07.02 | 75 | 285 | 3794 | 6.85 | 91.1 |
| O5 | 2001.08.01 | 47 | 82 | 1739 | 3.73 | 78.8 |
| O6 | 2001.09.10 | 22 | 72 | 3224 | 2.51 | 112.5 |
| O7 | 2001.10.15 | 199 | 93 | 469 | 3.93 | 19.7 |
| O8 | 2001.11.05 | 64 | 127 | 1972 | 4.64 | 71.9 |
| O9 | 2001.12.17 | 116 | 879 | 7556 | 6.77 | 58.1 |
| O10 | 2002.01.15 | 126 | 311 | 2467 | 5.27 | 41.7 |
| O11 | 2002.02.05 | 52 | 319 | 6100 | 3.39 | 64.7 |
| O12 | 2002.03.04 | - ^{a)} | 919 | - | 9.80 | - |
| | (GM) | 68.7 | 262.7 | 3412.8 | 5.2 | 72.2 |
| | (GSD) | 1.81 | 2.36 | 2.38 | 1.43 | 1.77 |
| Morioka | | | | | | |
| M1 | 2003.07.16 | - | 1.59 | - | 0.54 | - |
| M2 | 2003.07.16 | - | 1.87 | - | 0.54 | - |
| M3 | 2003.07.17 | - | 2.58 | - | 0.83 | - |
| M4 | 2003.07.17 | - | 2.26 | - | 0.73 | - |
| M5 | 2003.07.18 | - | 1.77 | - | 1.19 | - |
| M6 | 2003.07.18 | - | 1.63 | - | 1.13 | - |
| M7 | 2003.07.20 | - | 1.79 | - | 0.46 | - |
| M8 | 2003.07.20 | - | 2.54 | - | 0.52 | - |
| | (GM) | | 2.0 | | 0.7 | |
| | (GSD) | | 1.21 | | 1.45 | |

a) '-': not determined

PFOA concentrations in Oyamazaki were different by order of magnitude, compared to those in Morioka. Therefore, air in Oyamazaki seemed to have an intensive source of PFOA. Given the heavy traffic, the most likely source would be particulate matters in motor vehicle emission, and/or those that rubbed off from automobiles. Another possible source could be particular matters blown from the road. It is known that Teflon[®] that contains PFOA in the manufacturing process, is employed widely for automaking, for example, in paint sealant coating, oil additives, brake parts, grease, and for soil caking agents used for road improvement, specifically, control of dust.

We reported previously that estimated human exposure to PFOS through inhalation was little compared that via drinking water based on the

pharmacokinetic model (Harada et al. 2003; Sasaki et al. 2003). Such intensive PFOA contamination of the air in Oyamazaki might affect the exposure to PFOA in Kyoto. Assuming that adult humans inhale 15 m³ of air per day, all dusts are respirable—i.e., their aerodynamic diameters are between 1 - 10 µm—and the PFOA inhaled on dust particles was absorbed completely into the body, the daily intake is estimated at 29.5 pg/day in Morioka City and 3.9 ng/day in Oyamazaki. The value in Oyamazaki is close to estimated daily intake of PFOA through tap water in Kyoto—10.8 ng/day as the concentration of 5.4 ng/L is multiplied by daily water intake of 2 L/day (Saito et al. 2004). If so, the exposure intensity from respiration would account for 36% at most in Kyoto and is not negligible.

The limitation of the present study is that we did not evaluate the concentrations of PFOA and PFOS focused on particulate size. This means that the present exposure dose by inhalation is overestimated. Therefore, the argument on exposure dose levels needs to be interpreted cautiously. We believe that such a large level of exposure should be assessed correctly and warrants further study.

This paper shows evidence suggesting that the level of air-borne PFOA, unlike PFOS, is considerably high in Oyamazaki, Kyoto. Further studies are necessary to investigate the source of PFOA, in order to clarify the environmental source of the PFOA in the Kinki area.

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